

This midterm consists of 5 consecutively numbered pages plus a formula sheet. Please check that your paper is complete before starting work. All work must be shown in this booklet.

Name: _____
(print, surname first)

Student number: _____

Signature: _____

Lecture Section: _____

University of British Columbia

Mid-term Examination

February 6, 2012

CHEMISTRY 205

Physical Chemistry

Time: 60 minutes

Answer all questions

NON-PROGRAMMABLE NON-GRAPHING CALCULATORS ARE PERMITTED

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READ AND OBSERVE THE FOLLOWING EXAM RULES

1. Each candidate must be prepared to produce, upon request, a UBCcard for identification.
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Question	Max	Mark
1	10	
2	10	
3	10	
Total	30	

SOME FAMILIAR EQUATIONS and CONSTANTS:

NOTE: conditions to which they apply are NOT specified here.

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$k = 1.3807 \times 10^{-23} \text{ JK}^{-1}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$$

$$F = eN_A = 96485 \text{ C mol}^{-1}$$

$$c = 2.998 \times 10^8 \text{ m/s}$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$1 \text{ atm} = 101325 \text{ Pa}$$

$$\left(p + a \frac{n^2}{V^2}\right)(V - nb) = nRT$$

$$\Delta U = U_2 - U_1 = q + w$$

$$dw = -p_{\text{ex}} dV$$

$$w = -p_{\text{ex}}(V_2 - V_1)$$

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$dq = C dT$$

$$nC_{V,m} = (dq_V / dT)$$

$$(\Delta U)_V = q_V = \int_{T_1}^{T_2} nC_{V,m} dT$$

$$H = U + pV$$

$$nC_{p,m} = (dq_p / dT)$$

$$(\Delta H)_p = q_p = \int_{T_1}^{T_2} nC_{p,m} dT$$

$$C_{V,m} = \frac{3}{2}R \quad C_{p,m} = \frac{5}{2}R$$

$$dS = dq_{\text{rev}}/T$$

$$S = k \ln W$$

$$\Delta S = S_2 - S_1 = \int_{\text{state1}}^{\text{state2}} (dq_{\text{rev}}/T)$$

$$\Delta S = nC_{V,m} \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$$

$$(\Delta S)_p = nC_{p,m} \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{surr}}$$

$$\ln \frac{p_2}{p_1} = -\frac{\Delta_{\text{vap}} H_m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$G = H - TS$$

$$F = C - P + 2$$

$$\Delta_r G = \Delta_r G^0 + RT \ln(Q)$$

$$E = -\frac{\Delta_r G^0}{n \cdot F} - \frac{R \cdot T}{n \cdot F} \cdot \ln(Q)$$

$$= E^0 - \frac{R \cdot T}{n \cdot F} \cdot \ln(Q)$$

$$\Delta T_b = T_{b,\text{mix}} - T_{b,\text{pure}} \approx K_b b_B = K_b m_B$$

$$\Delta T_f = T_{f,\text{mix}} - T_{f,\text{pure}} \approx -K_f b_B = -K_c m_B$$

$$\Pi = c_B RT$$

$$\varepsilon \approx -\frac{RT}{z_i F} \ln\left(\frac{[i]_R}{[i]_L}\right)$$

$$\Delta \Pi = \Delta c RT$$

$$c = \lambda \nu$$

$$\Delta E = h \nu = h c / \lambda$$

$$T = I / I_0$$

$$A = \log_{10}(I_0 / I) = \varepsilon c l$$

$$E_{\text{vib}} = \hbar \sqrt{\frac{k}{\mu}} \left(\nu + \frac{1}{2}\right)$$

$$[A] = [A]_0 - k t \quad \text{and} \quad t_{1/2} = [A]_0 / (2k)$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -k t \quad \text{and} \quad t_{1/2} = (\ln 2) / k$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k t \quad \text{and} \quad t_{1/2} = \frac{1}{k[A]_0}$$

$$k = A \exp(-E_a / (RT))$$

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\nu = \frac{\nu_{\text{max}} [S]}{[S] + K_M}$$

1. [10 marks] In each part of this question give your answer in the box. There is only one correct answer for each part.

(a) Which of the following sets of conditions will never give rise to a spontaneous (irreversible) process under constant pressure and constant temperature?

- i. positive ΔH and positive ΔS
- ii. positive ΔH and negative ΔS
- iii. negative ΔH and positive ΔS
- iv. negative ΔH and negative ΔS

(b) Two moles of an ideal monatomic gas is confined within a two-dimensional plane at constant temperature T . What is the internal energy of this system according to the equipartition rule which arose from our discussion of the kinetic model?

- i. RT
- ii. $1.5RT$
- iii. $2RT$
- iv. $2.5RT$
- v. $3RT$

(c) When the temperature of a system decreases, which of the following statements is true?

- i. All molecules in this system move faster.
- ii. All molecules in this system move slower.
- iii. The average molecular speed is smaller.
- iv. The average molecular speed is larger.
- v. All molecules maintain the same velocity.

(d) For a constant-volume process in a closed system, $\Delta H = \Delta U$ always.

- i. True
- ii. False

(e) According to Gibbs, ΔG alone can predict the spontaneity of any process under all conditions.

- i. True
- ii. False

(f) For a general process in an isolated system, the following is always true:

- i. $\Delta S = 0$
- ii. $\Delta G = 0$
- iii. $\Delta U = 0$
- iv. $\Delta H = 0$
- v. $q = 0$

(g) A sample of an ideal gas, contained within a closed vessel, undergoes some process starting from 1 atm and 2 L and arriving at 4 atm and 0.5 L. Which of the following statements is always true for every possible path?

- i. During the entire process, T is a constant.
- ii. During the entire process, U is a constant.
- iii. During the entire process, H is a constant.
- iv. $\Delta H = H_{\text{final}} - H_{\text{initial}} = 0$.
- v. $q > 0$.

(h) Thermodynamics not only tells us the direction a process will proceed, but also the rate of the process.

- i. True
- ii. False

(i) According to the second law, any irreversible process taking place in the universe always increases the entropy of the system.

- i. True
- ii. False

(j) The entropy change in an irreversible process between two states ($\Delta S \equiv S_f - S_i$) satisfies

$$\Delta S > \int_i^f \frac{dq}{T}$$

- i. True
- ii. False

2. [10 marks]

- (a) Calculate q , w , ΔU , ΔH , ΔS , ΔG , $\Delta S_{\text{universe}}$ for the reversible, isothermal expansion at 300 K of 5.00 mol of a perfect gas from 0.5 L to 1.5 L.

variable	value	units
w	<input type="text"/>	J
q	<input type="text"/>	J
ΔU	<input type="text"/>	J
ΔH	<input type="text"/>	J
ΔS	<input type="text"/>	J/K
ΔG	<input type="text"/>	J
$\Delta S_{\text{universe}}$	<input type="text"/>	J/K

- (b) Is this process reversible, irreversible or impossible?

i. Irreversible

ii. Reversible

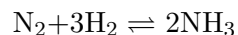
iii. Impossible

- (c) What would ΔU and w be if the expansion connects the same initial and final states as in (a) but is done by having the perfect gas expand into a vacuum?

ΔU	<input type="text"/>	J
w	<input type="text"/>	J

3. [10 marks]

(a) Consider the following gas-phase chemical reaction



- i. [2 marks] The equilibrium constant K is 477978 at 298 K. Calculate the Standard Gibbs energy of reaction at 298 K.
- ii. [3 marks] For the same reaction, $\Delta S^0 = -200 \text{ J K}^{-1}\text{mol}^{-1}$ and $\Delta H^0 = -92 \text{ kJ/mol}$. Assuming that ΔS^0 and ΔH^0 are independent of temperature, calculate the equilibrium constant at 460 K.
- iii. [1 mark]
A chemist wants to produce ammonia (NH_3) at 460 K in a reservoir containing H_2 , N_2 and NH_3 . Initially each gas has a partial pressure of 1 atm. What does the chemist need to do in order to produce more ammonia?
- A. Reduce the nitrogen pressure
B. Increase the hydrogen pressure
C. increase the ammonia pressure
D. Change nothing
- (b) [4 marks] What measurements would you perform to extract $\Delta_{\text{rxn}}H^0$ (the change in molar enthalpy in a chemical reaction) and $\Delta_{\text{rxn}}S^0$ (the change in molar entropy in a chemical reaction) assuming that $\Delta_{\text{rxn}}H^0$ and $\Delta_{\text{rxn}}S^0$ are independent of temperature. Hint: recall $\Delta G^0 = -RT \ln K$

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(c) Which of the following sets of conditions will never give rise to a spontaneous (irreversible) process under constant pressure and constant temperature?

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(d) Two moles of an ideal monatomic gas is confined within a two-dimensional plane at constant temperature T . What is the internal energy of this system according to the equipartition rule which arose from our discussion of the kinetic model?

- i. $3RT$
- ii. $2.5RT$
- iii. $2RT$
- iv. $1.5RT$
- v. RT

(e) The entropy change in an irreversible process between two states ($\Delta S \equiv S_f - S_i$) satisfies

$$\Delta S > \int_i^f \frac{dq}{T}$$

- i. True
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- (f) According to Gibbs, ΔG alone can predict the spontaneity of any process under all conditions.
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 - v. $\Delta G = 0$
- (j) According to the second law, any irreversible process taking place in the universe always increases the entropy of the system.
- i. True
 - ii. False

2. [10 marks]

- (a) Calculate q , w , ΔU , ΔH , ΔS , ΔG , $\Delta S_{\text{universe}}$ for the reversible, isothermal expansion at 400 K of 2.00 mol of a perfect gas from 0.4 L to 1.2 L.

variable	value	units
w	<input type="text"/>	J
q	<input type="text"/>	J
ΔU	<input type="text"/>	J
ΔH	<input type="text"/>	J
ΔS	<input type="text"/>	J/K
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- (b) Is this process reversible, irreversible or impossible?

i. Irreversible

ii. Reversible

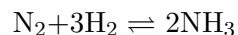
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Chem 205 midterm answers 2012

Q1	♥	♦
a	i	ii
b	ii	iii
c	iii	iii
d	iii	ii
e	i	ii
f	ii	v
g	v	iv
h	ii	ii
i	i	ii
j	ii	i
Q2 a		
w	-7307	-13701
q	7307	13701
ΔU	0	0
ΔH	0	0
ΔS	18.27	45.67
ΔG	-7307	-13701
$\Delta S_{\text{universe}}$	0	0
Q2 b	ii	ii
Q2 c		
ΔU	0	0
w	0	0
Q3		
a	-32400 J/mol	-32400 J/mol
b	1	1
c	B	B
d		